



## Short communication

## Rechargeable hybrid aqueous batteries

Jing Yan, Jing Wang, Hao Liu, Zhumabay Bakenov<sup>1</sup>, Denise Gosselink, P. Chen\*

Department of Chemical Engineering, Faculty of Engineering and Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

## H I G H L I G H T S

- New concept in rechargeable aqueous batteries.
- Deposition/dissolution anode and intercalation cathode in aqueous electrolyte.
- Energy storage system with large capacity retention and long cycle life.
- Alternative to commercial lead-acid batteries and for load leveling applications.

## A R T I C L E I N F O

## Article history:

Received 15 May 2012

Accepted 18 May 2012

Available online 29 May 2012

## Keywords:

Aqueous electrolyte

Electrochemistry

Intercalation

Metal electrode

Rechargeable battery

## A B S T R A C T

A new aqueous rechargeable battery combining an intercalation cathode with a metal (first order electrode) anode has been developed. The concept is demonstrated using  $\text{LiMn}_2\text{O}_4$  and zinc metal electrodes in an aqueous electrolyte containing two electrochemically active ions ( $\text{Li}^+$  and  $\text{Zn}^{2+}$ ). The battery operates at about 2 V and preliminary tests show excellent cycling performance, with about 90% initial capacity retention over 1000 charge–discharge cycles. Use of cation-doped  $\text{LiMn}_2\text{O}_4$  cathode further improves the cyclability of the system, which reaches 95% capacity retention after 4000 cycles. The energy density for a prototype battery, estimated at 50–80 Wh  $\text{kg}^{-1}$ , is comparable or superior to commercial 2 V rechargeable batteries. The combined performance attributes of this new rechargeable aqueous battery indicate that it constitutes a viable alternative to commercial lead-acid system and for large scale energy storage application.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

The eminent global energy crisis and growing ecological concerns in the past two decades has led to intensive development in the fields of green transportation such as electric and hybrid electric vehicles, as well as clean energy sources such as wind and solar power. These technologies demand low cost, safe, and environmentally friendly energy storage systems. Batteries are versatile means of storing electricity in the form of chemical energy and many technologies, such as lead-acid, nickel–cadmium (Ni–Cd), nickel-metal hydride (Ni–MH), redox flow-cells (RFCs) and lithium ion batteries (LIBs), are commercially available or under intense research [1–5]. Drawbacks in these systems still hinder their utilization for large-scale energy storage: Ni–Cd and lead–acid batteries present serious ecological threat due to the highly poisoning metals lead and cadmium; lead–acid has short

cycle life; Ni–MH is expensive mostly due to low abundance of the precursors for anode material; and the rather complicated flow-cells provide lower energy densities than portable batteries. LIBs can afford quite large energy densities but it employs organic electrolytes made with highly toxic and flammable solvents and its manufacture is complicated and expensive, partly because the electrolyte is moisture and air sensitive. Incorporation of aqueous electrolytes in rechargeable lithium batteries tackles these safety, economical, and environmental issues. Aqueous electrolytes, despite having a narrower electrochemical stability window than their organic counterparts (2–2.5 V instead of 3–5 V), are safer, less toxic, and demand simpler, less stringent manufacturing environments. In 1994, Dahn and co-workers proposed an aqueous based “rocking-chair” type battery using  $\beta\text{-VO}_2$  and  $\text{LiMn}_2\text{O}_4$  as negative and positive electrodes, respectively [6]. Despite of its poor cyclability, the prospects of that system instigated many studies of similar aqueous rechargeable lithium-ion batteries, ARLBs [7–11]. A recent report presented a  $\text{LiTi}_2(\text{PO}_4)_3/\text{LiSO}_4/\text{LiFePO}_4$  aqueous battery with improved cycling stability [12]. By eliminating  $\text{O}_2$ , controlling the electrolyte pH, and carbon-coating the electrode materials, the system maintained 90% of its initial capacity after 1000 cycles at high current rates. Nonetheless, it showed inferior

\* Corresponding author. Tel.: +1 519 888 4567; fax: +1 519 888 4347.

E-mail address: [p4chen@uwaterloo.ca](mailto:p4chen@uwaterloo.ca) (P. Chen).URL: <http://chemeng.uwaterloo.ca/faculty/chen.html><sup>1</sup> Present Address: School of Engineering, Nazarbayev University, Kabanbay batyr Ave., 53, Astana 010000, Kazakhstan.

cycling stability at lower rates and considerable capacity fading. The authors concluded that the instability of discharged anode materials in water, especially in the presence of oxygen, is the primary reason for the capacity fading in ARLBs. This indicates that a fundamentally different approach is needed in the selection of anode materials for lithium aqueous batteries. Alternatively, rechargeable Zn/MnO<sub>2</sub> batteries have been extensively studied for several decades but its practical application is restricted by the poor reversibility of the cathodic reaction. The electrochemical behavior of Zinc in acidic solutions ( $\text{Zn} \leftrightarrow \text{Zn}^{2+}$ ) is markedly different from that in neutral or alkaline electrolytes ( $\text{Zn(OH)}_2$ ,  $\text{ZnO}_2^{2-}$ ,  $[\text{Zn(OH)}_4]^{2-}$  being formed depending on potential and pH value) [13–15]. Minakshi et al. showed that reversibility can be achieved by substituting  $\text{LiMnPO}_4$  for the  $\text{MnO}_2$  cathode and using an aqueous  $\text{LiOH/ZnSO}_4$  electrolyte solution; however, the utilization of the cathode material was relatively low due to the high pH of the electrolyte [13]. On the other hand, although the electrochemical stability window of pure water is only 1.23 V, lower pH values result in higher potential for O<sub>2</sub> evolution, which in turn can improve the utilization of cathode materials. In spite of that, the literature data on aqueous Li(Host) batteries is limited to neutral or alkaline electrolytes. Recently, good cycling stability was reported for a zinc ion battery (ZIB) based on Zn anode and  $\alpha\text{-MnO}_2$  cathode and a mild aqueous electrolyte solution of zinc salt [16]. Here we report on a new  $\text{LiMn}_2\text{O}_4/\text{ZnCl}_2 + \text{LiCl/Zn}$  aqueous rechargeable battery which operates in mildly acidic aqueous electrolyte and shows high Coulombic efficiency as well as long cycle life.

## 2. Experimental

Composite cathodes were prepared by casting slurries of  $\text{LiMn}_2\text{O}_4$  (undoped and doped materials from MTI Co. and Wuxi Jewel Power & Materials Co., Ltd., respectively), acetylene black (Alfa Aesar Co.), and polyvinylidene fluoride (PVDF, Arkema Inc.) (83:10:7 wt.%) in *n*-methyl-2-pyrrolidinone (NMP, Sigma–Aldrich Co.) on graphite foil (SGL Group Co.), and air drying at 110 °C for 24 h. Disks of 12 mm diameter were cut (typical active material load of 2.4 mg cm<sup>-2</sup>) and soaked in the electrolyte solution under reduced pressure. A 12 mm in diameter stainless steel rod (SUS316) was used as an anode current collector in charge–discharge cycling tests. The electrolyte was prepared by dissolving 3 mol dm<sup>-3</sup> LiCl and 4 mol dm<sup>-3</sup>  $\text{ZnCl}_2$  (both Aldrich) in deionized water and adjusting the solution to pH = 4 by titration with 0.1 mol dm<sup>-3</sup> LiOH. AGM (Absorbed Glass Mat, NSG Corporation) wet with the electrolyte was used as separator. Two-electrode Swagelok™-type cells were used for galvanostatic charge–discharge cycling at room temperature by means of a battery tester (Arbin Instruments Co) at various C-rates calculated based on the practical specific capacity of undoped  $\text{LiMn}_2\text{O}_4$  spinel (1 C = 130 mAh).

Cyclic voltammetry (CV) was performed with a VMP3 potentiostat/galvanostat (Bio-Logic Science Instruments Co.) in a three-electrode Swagelok™-type cell at 0.5 mV s<sup>-1</sup> scan rate in various voltage ranges (–0.5–2.4 V vs.  $\text{Zn}^{2+}/\text{Zn}$ ), using  $\text{LiMn}_2\text{O}_4$  composite or glassy carbon, platinum, and metallic zinc as working, counter, and reference electrodes, respectively. Zinc was omitted from the electrolyte for the evaluation of the electrolyte stability window to allow for distinction between hydrogen evolution and zinc deposition processes in the anode.

The chemical stability of undoped and doped  $\text{LiMn}_2\text{O}_4$  in electrolyte solutions with pH 1 and 4 was evaluated by measuring the concentration of  $\text{Mn}^{2+}$  ions in 0.1 dm<sup>3</sup> of electrolyte in contact with 10 g of active material for different periods of time. 0.001 dm<sup>3</sup> aliquots collected from the electrolyte were diluted to 0.01 dm<sup>3</sup> and analyzed by Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Teledyne–Leeman, Prodigy Radial). The separator of

one cell cycled for 130 cycles was immersed in 10 cm<sup>3</sup> deionized water, which was stirred for 24 h. After filtration, it was also analyzed via ICP-OES. The system was standardized from 0 to 160 mg L<sup>-1</sup> for each metal analyte and yttrium was used as an internal standard at a fixed concentration of approximately 10 mg L<sup>-1</sup> throughout. A weighted-linear curve fit was used for quantification. The lower limit of detection (LLOD) was calculated as 3 times the standard deviation of 20 blank (pure water) determinations.

Powder x-ray diffraction (XRD) patterns were collected using D8 Discover (Bruker Co.,  $\text{CuK}\alpha$  1.5406 Å, 40 kV, and 40 A) equipped with LynxEye detector, at scan rates of 2° min<sup>-1</sup> for the anode (*ex-situ* before and after charge) and 1° min<sup>-1</sup> for the cathode (*in situ* during relaxation period after the reaction of every 0.25 mol of Li, using a Kapton™ pouch cell cycled galvanostatically at 2 C rate with a Neware CT-3008W battery tester).

## 3. Results and discussion

The performance of a rechargeable battery greatly depends on the properties of the electrode and electrolyte materials, which must be selected according to specific requirements as depicted in Fig. 1. Large potential differences between the electrodes give higher power output but, due to environmental and sustainability concerns, the ideal materials for a battery should be abundant and of low-toxicity which will ultimately influence the manufacture process and economy of a battery. A long cycle life, desirable for a rechargeable battery, is dictated by the reversibility of the redox reactions, the stability of both electrodes in the electrolyte, and of the electrolyte itself. The volume changes occurring upon cycling greatly influences the reversibility in intercalation materials. However, the aforementioned stability issues of intercalation compounds with suitable redox potential (e.g. carbon,  $\text{LiV}_3\text{O}_8$ ,  $\text{TiP}_2\text{O}_7$ ,  $\text{LiTi}_2(\text{PO}_4)_3$ ) prevent their use as anode materials in ARLBs [12]. Alternatively, first order electrodes undergo highly reversible redox deposition/dissolution in aqueous electrolytes. The reversibility of these processes in aqueous media depends on the reduction potential of the metal, solution pH, and the over-potential for hydrogen evolution on the metal. Consequently, among the metals presented in Fig. 1, zinc is the most suitable anode material for an aqueous battery: it exhibits low redox potential, good reversibility, high over-potential for hydrogen evolution in acidic solutions [17], and large specific capacity (820 mAh g<sup>-1</sup>). In terms of cathode materials, both spinel  $\text{LiMn}_2\text{O}_4$

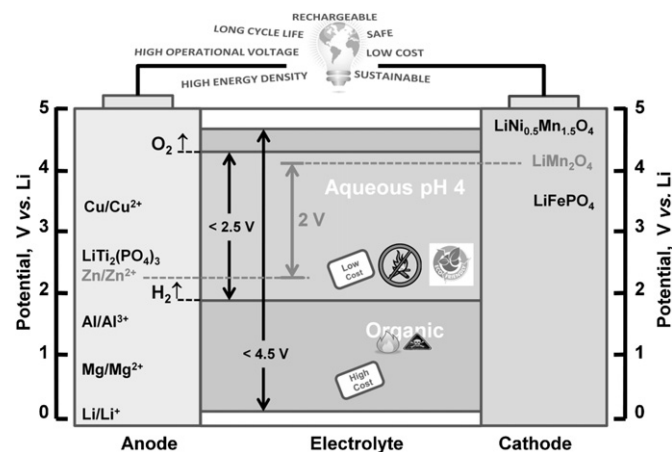


Fig. 1. Desired characteristics of cell components and resulting cell performance. Both aqueous and organic electrolyte stability windows, as well as the operation voltage range of the Zn/ $\text{LiMn}_2\text{O}_4$  ReHAB, are shown for comparison.

and olivine  $\text{LiFePO}_4$  may be employed in aqueous batteries, the former providing higher energy density due to its higher redox potential compared to that of  $\text{LiFePO}_4$ .  $\text{LiMn}_2\text{O}_4$  also exhibits only about 7% volume variation between lithiated and non-lithiated forms, which is much lower than the 90% observed in the  $\text{PbO}_2$  electrodes of lead–acid batteries [18,19] and hybrid supercapacitors using  $\text{LiMn}_2\text{O}_4$  cathode in aqueous electrolyte achieve up to 20,000 cycles without significant capacity decay [20]. In practice, the cyclability of  $\text{LiMn}_2\text{O}_4$  electrodes is limited by its dissolution into the electrolyte [21–24], which can be thwarted by chemical doping and surface coating [25]. The redox potential of  $\text{LiMn}_2\text{O}_4$  depends on the concentration of lithium ions and does not change markedly with the electrolyte pH. Furthermore, in aqueous solutions with pH lower than 9, lithium de/intercalation in  $\text{LiMn}_2\text{O}_4$  occurs at potentials below that for oxygen evolution (the upper limit of the electrolyte stability window).

Consideration of the above indicates that zinc and  $\text{LiMn}_2\text{O}_4$  are suitable electrodes for a rechargeable aqueous battery with an output voltage of about 2 V. Upon charge of this electrochemical cell, lithium extraction from the cathode occurs only if zinc ions are present in solution to be reduced at the anode, which also ensures the electrolyte charge neutrality. Therefore, the electrolyte was formulated by dissolving both  $\text{Li}^+$  and  $\text{Zn}^{2+}$  salts (for detailed assessment of the electrolyte composition, see the [Supplemental Information, SI](#)). The dissolution of  $\text{Mn}^{2+}$  into organic and aqueous electrolyte, resulted by the disproportionation reaction:  $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$  which is accelerated in the presence of acids such as HF, is a factor known to cause capacity fading of  $\text{LiMn}_2\text{O}_4$  [26]. In order to determine the stability of cathode material in the aqueous electrolyte we analyzed the Mn content in the solution stored for one week in the presence of undoped and doped  $\text{LiMn}_2\text{O}_4$ . The ICP results (Table 1) show that, at pH 1 considerable amount of manganese is dissolved whereas, at pH 4, less than  $4 \text{ mg L}^{-1}$  of Mn ions were found in the electrolytes. Accordingly, only  $0.05 \text{ mg L}^{-1}$  of Mn ions was detected in the electrolyte after 130 cycles, in agreement with the literature values [27]. These results confirm the higher stability of the doped material and suggest that, although Mn dissolution can occur in an aqueous electrolyte with the composition employed, it does not seem to cause any deleterious effects on the cyclability of our system other than reduction in capacity. Further investigation on the extent of cathode dissolution and its effects on cycling stability and storage properties of the system are underway.

The typical galvanostatic charge–discharge profiles of a Zn/ $\text{LiMn}_2\text{O}_4$  cell are depicted in Fig. 2a, showing the two-phase lithium extraction/intercalation behavior inherent to spinel  $\text{LiMn}_2\text{O}_4$  [24,28,29]. Cells assembled with both undoped and cation-doped  $\text{LiMn}_2\text{O}_4$  cathode were cycled at 4C rate revealing excellent cycling performance. Cells with undoped  $\text{LiMn}_2\text{O}_4$  cathode (Fig. 2b) retain near 90% of the initial capacity after 1000 cycles, suggesting few detrimental side reactions upon cycling, a desirable trait for a rechargeable battery. The Coulombic efficiency fades along with the discharge capacity since the batteries were cycled using a capacity limited charging protocol. Similar voltage profiles are observed for the 1st, 100th and 1000th cycles (Fig. 2a), with a slight increase in polarization. Use of doped  $\text{LiMn}_2\text{O}_4$  further improves

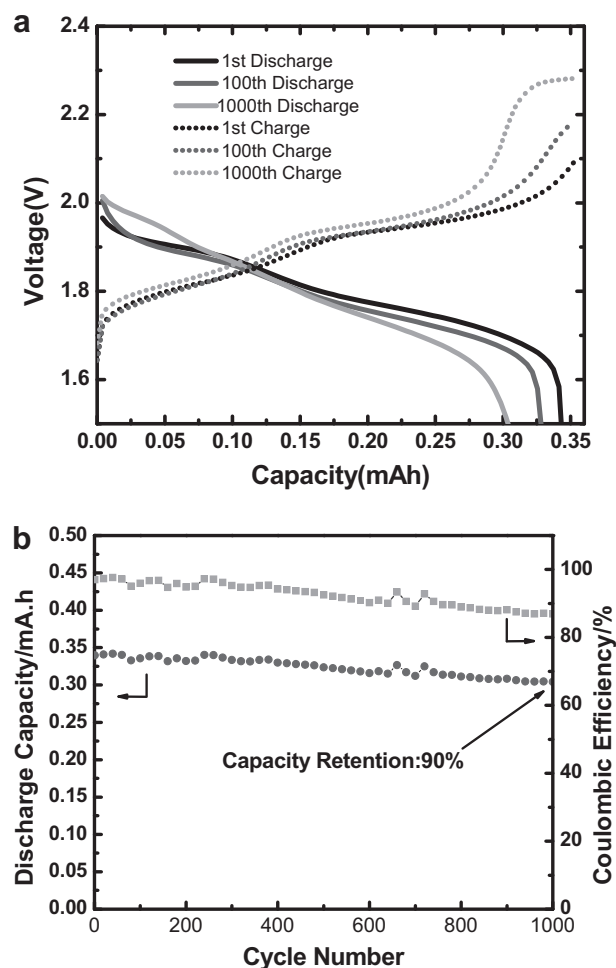


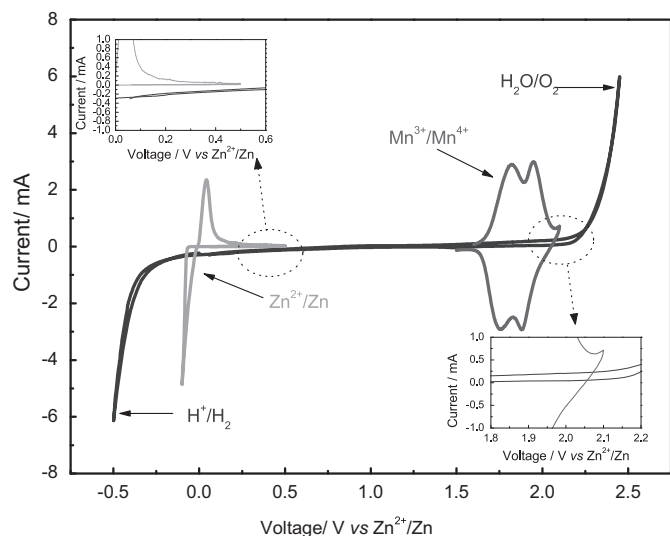
Fig. 2. Electrochemical performance of the Zn/ $\text{LiMn}_2\text{O}_4$  cell. (a) Charge-discharge profiles for different cycles of a cell operated at 4 C rate ( $1.1 \text{ mA cm}^{-2}$ ); (b) cyclability and coulombic efficiency of undoped  $\text{LiMn}_2\text{O}_4$ .

the system's capacity retention to up to 95% after 4000 cycles (Fig. S4). To our knowledge, this is an unprecedented performance for rechargeable aqueous batteries with  $\text{LiMn}_2\text{O}_4$  cathode at such high cycling rates and may indicate successful overcome of the anode instability issues in aqueous electrolytes. These results demand comprehensive investigation of the mechanism involved during battery operation. The CV data obtained at various potential ranges versus  $\text{Zn}^{2+}/\text{Zn}$  electrode are presented in Fig. 3 and demonstrate the characteristic potentials of the redox processes in the studied system. Along with the investigation of the processes reversibility, these data enable the evaluation of the electrochemical stability window of the electrolyte within the studied potential regions. The two sets of reversible processes observed at about 0 and 1.76–1.9 V are attributed to the reversible deposition/dissolution of zinc and the two-phase lithium extraction/intercalation in spinel  $\text{LiMn}_2\text{O}_4$  [24]. The two significant irreversible processes, one cathodic at  $-0.5 \text{ V}$  and one anodic at  $2.2 \text{ V}$ , can be assigned to hydrogen and oxygen evolution, respectively, due to decomposition of water in the electrolyte, indicating the limits of stability of the electrolyte (electrochemical stability window). These results confirm that the chosen combination of the electrodes,  $\text{LiMn}_2\text{O}_4$  and zinc metal, and electrolyte composition provide favorable conditions for efficient battery operation within the stability window of the electrolyte. Because of the remarkable difference in both ionic and electronic conductivities of the metallic

Table 1  
Concentration of Mn ions in electrolyte solution after exposure to  $\text{LiMn}_2\text{O}_4$  for 1 week.

Sample	Undoped $\text{LiMn}_2\text{O}_4$		Doped $\text{LiMn}_2\text{O}_4$		Cycled battery <sup>a</sup>
Electrolyte pH	1	4	1	4	4
Mn Concentration (mg/L)	204.8720	3.7000	179.2780	1.7220	0.0520

<sup>a</sup> Electrolyte collected from cell cycled for 130 cycles at 1C rate.



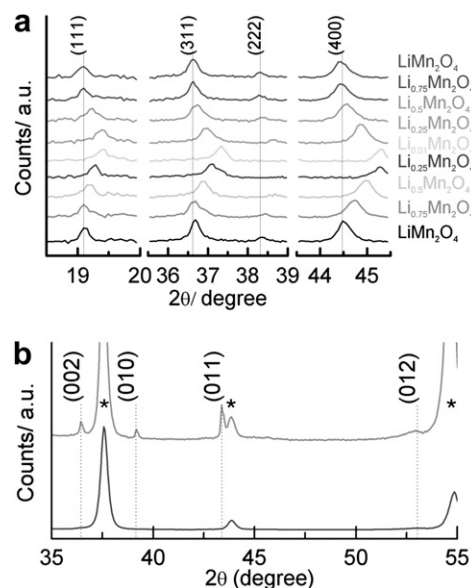
**Fig. 3.** CV data of the Zn/LiMn<sub>2</sub>O<sub>4</sub> system in aqueous electrolyte at scan rate of 0.5 mV s<sup>-1</sup>: anode (green); cathode (red); and electrochemical stability window of electrolyte (blue).

zinc anode and LiMn<sub>2</sub>O<sub>4</sub> cathode, the current density during the anodic reaction is much higher than that of the cathodic process. Thus, the latter is the kinetically limiting process during the battery operation. This implies that the C rate performance of this system is limited by the cathode material and we are in the process of enhancing its kinetic properties.

The XRD analysis of the electrodes before and during cycling allows for identification of the reaction products and could be used to support the CV results. The patterns of the cathode material collected *in situ* upon cycling are depicted in Fig. 4a. During charge, the characteristic lines of the spinel LiMn<sub>2</sub>O<sub>4</sub> shift toward higher 2θ values, indicating Li<sup>+</sup> extraction and formation of Mn<sub>2</sub>O<sub>4</sub> [30]; on discharge, the reverse process takes place. The reversible deposition/dissolution of Zn on the stainless steel anode current collector during charge/discharge is also verified by XRD (Fig. 4b). The XRD data confirm the electrochemical processes occurring upon cycling: reversible Li<sup>+</sup> ion extraction/intercalation at the LiMn<sub>2</sub>O<sub>4</sub> cathode and the reversible metal deposition/dissolution at the anode. No other processes were detected by CV or XRD, indicating absence of detrimental side-reactions within the electrolyte electrochemical stability window, consistent with the excellent cyclability of the system.

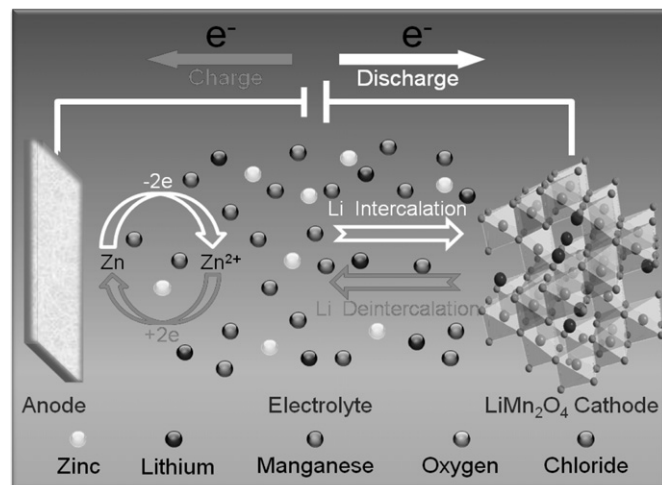
The mechanism elucidated by electrochemical and structural investigations is illustrated in Fig. 5. Contrary to the “rocking-chair” type batteries, exchange of lithium and zinc ions in the electrolyte occurs upon cycling. Hence, the electrolyte in this battery is more than an ionic conductive medium. It is also the source of anode, which is formed by zinc deposition upon charge process, being consumed and regenerated during the battery operation. Given the reversibility of the chemical reactions involved, the mechanism proposed explains the high coulombic efficiency and cycling stability reported here. Because of its asymmetric construction, metal anode and intercalation cathode, and the two types of chemistry involved in the electrodes upon cycling, deposition/dissolution and de-intercalation/intercalation, we refer to this system as a **Rechargeable Hybrid Aqueous Battery (ReHAB)**.

The energy density prospects for this battery are particularly attractive. Since the anode active material is Zn<sup>2+</sup> stored within the electrolyte, the specific gravimetric energy density depends mostly on the mass of the cathode and the minimum amount of electrolyte needed for the battery operation. For a 1 Ah prototype cell with



**Fig. 4.** Structural changes in the Zn/LiMn<sub>2</sub>O<sub>4</sub> ReHAB upon cycling: (a) *in-situ* XRD patterns of LiMn<sub>2</sub>O<sub>4</sub> cathode at various depths of charge and discharge during the first cycle and (b) *ex-situ* XRD patterns of stainless steel anode current collector before (blue) and after (red) charge; asterisk denotes the positions for the XRD lines of stainless steel.

30% w/w Zn<sup>2+</sup> excess the theoretical energy density is 160 Wh kg<sup>-1</sup>. Assuming that half of this value is lost when the weight of cell shell, electrolyte solvent, and other battery parts are considered (as it usually happens in lead–acid batteries), we estimate that the Zn/LiMn<sub>2</sub>O<sub>4</sub> ReHAB would deliver 50–80 Wh kg<sup>-1</sup> of practical energy density. This is much higher than that of lead–acid battery (about 30–50 Wh kg<sup>-1</sup>). Furthermore, this new battery system employs an environmentally friendly, and safer electrolyte and exhibits excellent cycle life, and the cell components are not air or/and moisture sensitive. Therefore, the ReHAB does not require expensive and strictly controlled assembly procedures and environment, as do LIBs. These key performance and economical advantages of the ReHAB allow us to suggest that this battery may be an alternative to the widely used lead–acid batteries. In addition, the ReHAB may potentially be used for large scale load leveling, which demands high energy efficiency, safety, long cycle life, and low cost.



**Fig. 5.** Schematic representation of the proposed mechanism for ReHAB operation.



Whilst we have shown the principle of the ReHAB operation in the Zn/LiMn<sub>2</sub>O<sub>4</sub> battery, this represents only one of such electrochemical cells; initial data of a system using LiFePO<sub>4</sub> as cathode is available in the [Supplemental Information \(SI\)](#). The ReHAB concept can be generally expressed as  $M/M^{x+}_{aq}, A^{y+}_{aq}/A(\text{Host})$ , where M is a metal and A is an intercalating ion. Consequently, sodium or magnesium ReHABs may be developed using stable metal anodes and appropriate intercalation cathode.

#### 4. Conclusions

A new rechargeable aqueous battery comprising a first order metal anode and an intercalation cathode has been developed. The battery operates via redox intercalation/deintercalation at cathode and metal ions deposition/dissolution at anode combined with the exchange of two kinds of cations in an aqueous electrolyte. The battery operation has been demonstrated using the Zn<sup>2+</sup>/Zn and LiMn<sub>2</sub>O<sub>4</sub>/Mn<sub>2</sub>O<sub>4</sub> redox couples. The system exhibits excellent cycling performance with capacity retention of 90% over 1000 cycles with undoped LiMn<sub>2</sub>O<sub>4</sub> and 95% over 4000 cycles with cation-doped LiMn<sub>2</sub>O<sub>4</sub>. Energy density estimations indicate that this technology can lead to 50–80 Wh kg<sup>−1</sup> net energy density in a prototype battery, making this new battery system a suitable energy storage alternative for large scale applications.

#### Acknowledgments

This research was financially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation (CFI), and the Canada Research Chairs (CRC) Program to one of the co-authors (PC). JY, JW, and PC acknowledge Dr. Haisheng Tao for useful discussions and assistance in experimental designs and ZB thanks Mr. Takayuki Fukada for help in performing electrochemical tests.

#### Appendix A. Supplementary material

Supplementary data related to this article can be found online at [doi:10.1016/j.jpowsour.2012.05.063](https://doi.org/10.1016/j.jpowsour.2012.05.063).

#### References

- [1] L.H. Taller, Electrically rechargeable redox flow cell, U.S. Patent 3,996,064, 1976.
- [2] J.L. Sudworth, A.R. Tilley, The Sodium–Sulfur battery, Chapman & Hall, New York, 1985.
- [3] A. Koenig, J. Rasmussen, Sandia Report SAND96–1062, 1996.
- [4] K.J. Cathro, K. Cedzynska, D.C. Constable, Journal of Power Sources 16 (1985) 53.
- [5] M. Wakihara, Materials Science and Engineering, R 33 (2001) 109.
- [6] W. Li, J.R. Dahn, D.S. Wainwright, Science 264 (1994) 1115–1118.
- [7] G.J. Wang, H.P. Zhang, L.J. Fu, B. Wang, Y.P. Wu, Electrochemistry Communications 9 (2007) 1873–1876.
- [8] H. Wang, Y. Zeng, K. Huang, S. Liu, L. Chen, Electrochimica Acta 52 (2007) 5102–5107.
- [9] J. Kohler, H. Makihara, H. Uegaito, H. Inoue, M. Toki, Electrochimica Acta 46 (2000) 59.
- [10] H. Wang, K. Huang, Y. Zeng, S. Yang, L. Chen, Electrochimica Acta 52 (2007) 3280–3285.
- [11] J.-Y. Luo, Y.-Y. Xia, Advanced Functional Materials 17 (2007) 3877.
- [12] J.-Y. Luo, W.-J. Cui, P. He, Y.-Y. Xia, Nature Chemistry 2 (2010) 760–765.
- [13] M. Minakshi, P. Singh, S. Thurgate, K. Prince, Electrochemical and Solid-State Letters 9 (2006) A471.
- [14] S. Barnartt, D.A. Forejt, Journal of the Electrochemical Society 111 (1964) C183.
- [15] F.R. McLarnon, E.J. Cairns, Journal of the Electrochemical Society 138 (1991) 645–664.
- [16] C. Xu, B. Li, H. Du, F. Kang, Angewandte Chemie International Edition 51 (2012) 933–935.
- [17] K.I. Popov, S.S. Djokić, B.N. Grgur, Fundamental Aspects of Electrometallurgy, Kluwer Academic/Plenum, New York, 2002.
- [18] T. Ohzuku, M. Kitagawa, T. Hirai, Journal of the Electrochemical Society 137 (1990) 769–775.
- [19] A. Czerwinski, M. Zelazowska, M. Grden, K. Kuc, J.D. Milewski, A. Nowacki, et al., Journal of Power Sources 85 (2000) 49–55.
- [20] Y.-G. Wang, J.-Y. Luo, C.-X. Wang, Y.-Y. Xia, Journal of the Electrochemical Society 153 (2006) A1425.
- [21] M. Thackeray, W. David, P. Bruce, J. Goodenough, Materials Research Bulletin 18 (1983) 461.
- [22] J. Goodenough, M.M. Thackeray, W. David, P. Bruce, Revue de Chimie Minerale 21 (1984) 435.
- [23] R.J. Gummow, A.D. Kock, M.M. Thackeray, Solid State Ionics 69 (1994) 59.
- [24] Z. Bakenov, I. Taniguchi, Solid State Ionics 176 (2005) 1027–1034.
- [25] T.-F. Yi, Y.-R. Zhu, X.-D. Zhu, J. Shu, C.-B. Yue, A.-N. Zhou, Ionics 15 (2009) 779–784.
- [26] J. Mun, S. Kim, T. Yim, J.H. Ryu, Y.G. Kim, S.M. Oh, Journal of the Electrochemical Society 157 (2010) A136–A141.
- [27] Q. Qu, L. Fu, X. Zhan, D. Samuelis, J. Maier, L. Li, et al., Energy & Environmental Science 4 (2011) 3985.
- [28] M.M. Thackeray, P.J. Johnson, L.A. de Piccolto, Materials Research Bulletin 19 (1984) 179.
- [29] R. Benedek, M.M. Thackeray, Solid-State Letters 9 (2006) A265.
- [30] K.-W. Nam, W.-S. Yoon, H. Shin, K.Y. Chung, S. Choi, X.-Q. Yang, Journal of Power Sources 192 (2009) 652–659.